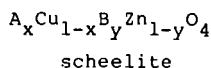
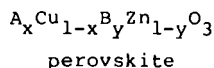


CRYSTAL AND CATALYTIC CHEMISTRY OF METHANOL SYNTHESIS

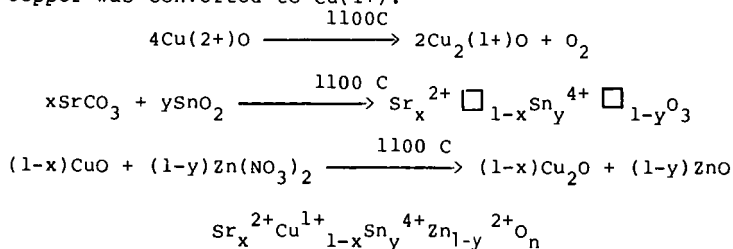
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Solid solutions of mixed metal oxides in the perovskite (ABO_3) and scheelite (ABO_4) families of crystals were used as host materials for the preparation of methanol synthesis catalysts. These materials contain a partial substitution of a copper (1+) ion in the A-sites of their structures and a Zn(2+) ion in their B-sites as homogeneous solid solutions in a host lattice containing at least two other metal oxides.



The synthesis of these unusual materials was accomplished by recognizing that copper oxides exist as an equilibrium mixture of Cu(1+) and Cu(2+) ions at temperatures in the range of 1100 C in air. Utilizing high temperature synthesis techniques, copper was disproportionated to a mixture of copper(2+) and copper(1+) oxides under oxidizing conditions. When this equilibrium mixture was exposed at high temperatures to a metal oxide composition containing a substoichiometric amount of the A-site cation, the equilibrium was shifted to copper(1+) which was incorporated into the A-site of the host. Due to the removal of Cu(1+) from the equilibrating system by its location in the stable A-site, all of the copper was converted to Cu(1+).



Support for the structure for these compounds was gained from an analysis of their magnetic susceptibility data, photoelectron spectra, x-ray diffraction data, and analytical analysis. The compounds were shown by the magnetic susceptibility data to be diamagnetic which was consistent with a d-10 copper(1+) ion. The absence of any shake-up structure in their ESCA spectra was

consistent only with a copper (1+) ion incorporated in the A-site of the solid state mixed metal oxide. Copper (2+) ions demonstrated large shakeup satellites in their ESCA spectra.

The objective of the synthesis of these novel materials was to provide a homogeneous solid solution of both the copper(1+) and zinc(2+) ions in the lattices of metal oxides which have unusual thermal and structural stability under reducing conditions. Using these materials which were then further modified by other ions substituted in the A- or B-sites, gradual electronic changes may be made in the copper(1+) ion. The solid solution, ion modified compounds will be subsequently used to understand the activation of carbon monoxide in methanol synthesis.

The activities of these materials as methanol synthesis catalysts were studied at 75 atm. and 230 C. The stabilities of the copper(1+) ions in the host lattices were examined between 200 C to 450 C in separate studies using diluted hydrogen in nitrogen. The methanol synthesis activities of these compounds when compared on a unit surface area basis were generally a bit lower than the copper modified zinc oxide catalysts prepared by coprecipitation. Their surface areas were substantially smaller than the Cu-Zn-O catalyst. In only a few cases was the stability of these solid state solutions toward reduction to copper(0) superior to that of the copper modified zinc oxide catalyst. This finding was surprising since one would expect the Cu(1+) atom of about 0.96 atomic radius to be configurationally stable from purely structural considerations. However, location of the mono-cation in a substantially greater electronegative lattice position contrasted to its solution in pure ZnO, may account for the observation of accelerated reduction in most examples using the complex solid state inorganics. A comparison of the relative rates of reduction of the solid state inorganic solutions to the coprecipitated standard Cu-Zn-O catalyst is shown in Figure 1. These data show that the metal ion composition may be used to regulate stability.

A study of the ease of reduction to metallic copper in a series of 10% metal ion modified copper zinc (25%/65%) oxide catalysts was performed. In addition a newly developed attrition test was used to examine the attrition resistance of these catalysts to mechanical wear. Ten percent concentrations of lanthanum, aluminum, magnesium, strontium, zirconium, tin, tungsten, molybdenum and chromium oxides were prepared with 25% copper oxide and 65% zinc oxide by coprecipitation. These modified compositions were found to be of superior mechanical strength when compared to unmodified 30% copper oxide-70% zinc oxide. In most cases the unmodified catalyst was reduced in hydrogen more easily than the modified ones. The solid state inorganic solutions of copper in the perovskite or scheelite crystals classes were substantially more attrition resistant than the modified copper zinc oxide systems.

FIGURE 1 RELATIVE DEGREES OF REDUCTION OF
 $\text{La}_{.8}\text{Cu}_{.2}\text{Nb}_{.8}\text{Zn}_{.2}\text{O}_{3.5}$, $\text{Cu}_{.73}\text{Zn}_{.27}\text{O}_x$, and $\text{Sr}_{.8}\text{Cu}_{.2}\text{Mo}_{.8}\text{Zn}_{.2}\text{O}_{3.5}$
 to copper zero at temperatures of 150°C to 450°C by 2% hydrogen in nitrogen
 at a gas hourly space velocity (GHSV) of 3500 hr^{-1} .

